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Characterization of Lorenz number with Seebeck coefficient measurement

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In analyzing zT improvements due to lattice thermal conductivity (κ_L) reduction, electrical conductivity (σ) and total thermal conductivity (κ_{Total}) are often used to estimate the electronic component of the thermal conductivity (κ_E) and in turn κ_L from $\kappa_L =\sim \kappa_{Total} - L\sigma T$. The Wiedemann-Franz law, $\kappa_E = L\sigma T$, where L is Lorenz number, is widely used to estimate κ_E from σ measurements. It is a common practice to treat L as a universal factor with 2.44×10^{-8} WΩK^{-2} (degenerate limit). However, significant deviations from the degenerate limit (approximately 40% or more for Kane bands) are known to occur for non-degenerate semiconductors where L converges to 1.5×10^{-8} WΩK^{-2} for acoustic phonon scattering. The decrease in L is correlated with an increase in thermopower (absolute value of Seebeck coefficient (S)). Thus, a first order correction to the degenerate limit of L can be based on the measured thermopower, $|S|$, independent of temperature or doping. We propose the equation: $L = 1.5 + \exp\left[-\frac{|S|}{116}\right]$ (where L is in 10^{-8} WΩK^{-2} and S in μV/K) as a satisfactory approximation for L. This equation is accurate within 5% for single parabolic band/acoustic phonon scattering assumption and within 20% for PbSe, PbS, PbTe, $Si_{0.8}Ge_{0.2}$ where more complexity is introduced, such as non-parabolic Kane bands, multiple bands, and/or alternate scattering mechanisms. The use of this equation for L rather than a constant value (when detailed band structure and scattering mechanism is not known) will significantly improve the estimation of lattice thermal conductivity. [http://dx.doi.org/10.1063/1.4908244]

A semiconductor with large Seebeck coefficient, high electrical conductivity, and low thermal conductivity is a good candidate for a thermoelectric material. The thermoelectric material's maximum efficiency is determined by its figure of merit $zT = \frac{S^2\sigma T}{\kappa_E+\kappa_L}$, where T, S, σ, κ_E, and κ_L are the temperature, Seebeck coefficient, electrical conductivity, and the electronic and lattice contributions to the thermal conductivity, respectively. Because the charge carriers (electrons in n-type or holes in p-type semiconductors) transport both heat and charge, κ_E is commonly estimated using the measured σ using the Wiedemann-Franz law: $\kappa_E = L\sigma T$, where L is the Lorenz number. Once κ_E is known, κ_L is computed by subtracting the κ_E from the total thermal conductivity, $\kappa_{Total} = \kappa_E + \kappa_L$. For this method, the bipolar thermal conductivity (κ_B) will also be included which can be written $\kappa_B + \kappa_L = \kappa_{Total} - L\sigma T$.

Since a high zT requires low κ_{Total} but high σ simultaneously, one of the more popular routes towards improving zT has been to reduce κ_L.[1] However, depending on the value of L, which maps

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from σ to κ_E, the resulting κ_L can often be misleading. For instance, in the case of lanthanum telluride, incautious determination of L can even cause κ_L to be negative, which is not physical.[2] Therefore, careful evaluation of L is critical in characterizing enhancements in zT due to κ_L reduction.

For most metals, where charge carriers behave like free-electrons, L converges to $\frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2 = 2.44 \times 10^{-8}$ WΩK^{-2} (degenerate limit). Although some heavily doped semiconductor thermoelectric materials have an L very close to the degenerate limit, properly optimized materials often have charge carrier concentrations between the lightly doped (non-degenerate) and heavily doped (degenerate) regions[3] ($\xi_{optimum}$ is near the band edge where ξ is the electronic chemical potential) which can result in errors of up to ~40%.[4]

Direct measurement of L[5] requires high mobility—typically beyond that attainable at the temperatures of interest (>300 K). Thus, L is typically estimated either as a constant (2.44×10^{-8} WΩK^{-2}) or by applying a transport model—such as the single parabolic band (SPB) model obtained by solving the Boltzmann transport equations—to experimental data.

For example, Larsen *et al.* proposed an approximate analytical solution of L based on the SPB model as a function of carrier concentration (n) and $(m^*T)^{-3/2}$ (where m^* is the effective mass) along with various sets of parameters for distinct carrier scattering mechanisms.[6] However, when the Hall carrier concentration, n_H, of a material is not available, the use of the approximate solution by Larsen is not possible. It can be shown that for the SPB model with acoustic phonon scattering (SPB-APS), both L and S are parametric functions of only the reduced chemical potential ($\eta = \xi/k_BT$, where k_B is Boltzmann constant); thus, no explicit knowledge of temperature (T), carrier concentration (n), or effective mass (m^*) is required to relate them.[7] We have utilized this correlation between L and measured S to estimate κ_L for a few known thermoelectric materials including: PbTe,[8–10] Zintl materials,[11–13] co-doped $FeV_{0.6}Nb_{0.4}Sb$ Half Heusler,[14] $La_{3-x}Te_4$,[2] resulting in much more satisfactory values for κ_L than the degenerate limit result ($L = 2.44 \times 10^{-8}$ WΩK^{-2}) would have.

While the SPB model works well to estimate L, a transcendental set of equations is needed to solve for L in terms of S—requiring a numerical solution. Considering that the typical measurement uncertainty for κ_{Total} is 10% and that SPB-APS is only an approximation, a much simpler equation would supply sufficient accuracy. Here, we propose the equation

$$L = 1.5 + \exp\left[-\frac{|S|}{116}\right] \tag{1}$$

(where L is in 10^{-8} WΩK^{-2} and S in μV/K) as a satisfactory approximation for L.

Equation (1) allows for a facile estimation of L from an experimental S only without requiring a numerical solution. We characterize the effectiveness of this estimate for L using some experimental data from relevant thermoelectric materials (PbSe,[15] PbS,[16] PbTe,[17,18] Zintl material (Sr_3GaSb_3),[11] Half Heusler (ZrNiSn),[19] and $Si_{0.8}Ge_{0.2}$[20]).

For a single parabolic band, L and S are both functions of reduced chemical potential (η) and carrier scattering factor (λ) only

$$L = \left(\frac{k_B}{e}\right)^2 \frac{(1+\lambda)(3+\lambda)F_\lambda(\eta)F_{\lambda+2}(\eta) - (2+\lambda)^2 F_{\lambda+1}(\eta)^2}{(1+\lambda)^2 F_\lambda(\eta)^2}, \tag{2}$$

$$S = \frac{k_B}{e}\left(\frac{(2+\lambda)F_{\lambda+1}(\eta)}{(1+\lambda)F_\lambda(\eta)} - \eta\right). \tag{3}$$

Where $F_j(\eta)$ represents the Fermi integral,

$$F_j(\eta) = \int_0^\infty \frac{\epsilon^j d\epsilon}{1 + \mathrm{Exp}[\epsilon - \eta]}. \tag{4}$$

By assuming that the carrier relaxation time is limited by acoustic phonon scattering (one of the most relevant scattering mechanisms for thermoelectric materials above room temperature[17,21]), Eqs. (2) and (3) can be solved numerically for L and the corresponding S as shown in Fig. 1 along with the proposed approximation (Eq. (1)).

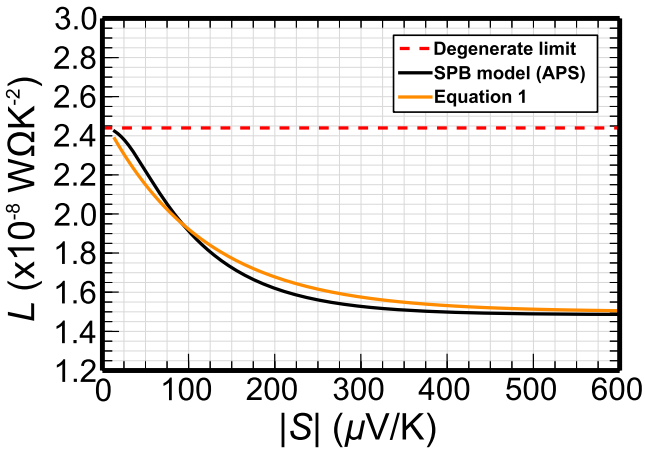

FIG. 1. Thermopower dependent Lorenz number calculated by the SPB model with APS and Eq. (1). For comparison, the degenerate limit of 2.44×10^{-8} WΩK^{-2} is also presented in a red dashed line.

According to the Fig. 1, the degenerate limit of L (2.44×10^{-8} WΩK^{-2}) is valid with errors less than 10% for materials whose thermopower is smaller than 50 μV/K (highly degenerate). In contrast, if the thermopower is large, the discrepancy with the degenerate limit can be up to 40%.

To decide an appropriate value of L with a known S easily, rather than graphically extracting it from Fig. 1, Eq. (1) can be used to quickly estimate L, given a measured thermopower. Equation (1) is accurate within 5% for single parabolic band where acoustic phonon scattering is dominant scattering mechanism when $|S| > \sim10$ μV/K. For $|S| < 10$ μV/K, while the SPB model converges to the degenerate limit, Eq. (1) increases exponentially, thus reducing the accuracy of the Eq. (1). Although estimation of L with an accuracy within 0.5% for SPB-APS is possible, this requires an approximate equation more complex than Eq. (1).[22]

Exceptions are known where L has been found to be outside the uncertainty described above for SPB-APS which are presented in Fig. 2 and Table I.[22] These exceptions typically involve either non-parabolic band structures (PbTe, PbSe, and PbS) or alternative scattering mechanisms (other than acoustic phonons). Narrow-gap semiconductors (lead chalcogenides, for example) are often better described by the non-parabolic Kane model which yields a different η dependence of L and S which depends on the non-parabolicity parameter: $\alpha = \frac{k_B T}{E_g}$ (E_g is the gap between conduction and valence band).[23,24] For well-studied lead chalcogenides (PbTe, PbSe, and PbS), a reasonable range

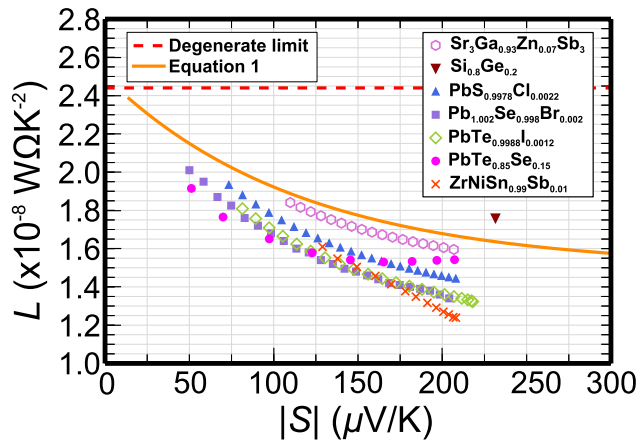

FIG. 2. Thermopower dependent Lorenz number obtained from materials whose band structure and scattering assumptions are different from those assumed in SPB-APS along with Eq. (1) calculation. For comparison, the degenerate limit of 2.44×10^{-8} WΩK^{-2} is also presented in a red dashed line.

TABLE I. Estimated maximum error to Eq. (1) for L with different band structure and scattering assumptions.

Band[a]	Scattering[b]	Examples	Maximum error (%)
P	AP	$Sr_3Ga_{0.93}Zn_{0.07}Sb_3$[11]	4.4
2P	AP + II	$Si_{0.8}Ge_{0.2}$[20]	7.5
K	AP	$PbTe_{0.9988}I_{0.0012}$[18]	19.7
K	AP + PO	$Pb_{1.002}Se_{0.998}Br_{0.002}$[15]	19.5
		$PbS_{0.9978}Cl_{0.0022}$[16]	19.4
K	AP + PO + AL	$ZrNiSn_{0.99}Sb_{0.01}$[19]	25.6
2K + P	AP	$PbTe_{0.85}Se_{0.15}$[17]	14.9

[a]Band is the type and number of bands involved in evaluating L. For instance, "2K + P" means two non-parabolic Kane bands (K) and a parabolic band (P).

[b]Scattering is the type of scattering mechanism assumed in estimating L. AP, II, PO, and AL are acoustic phonon, ionized impurities, polar, and alloy scattering, respectively. For example, "AP + PO" means that both acoustic phonon and polar scatterings are assumed in calculating L.

of α is from 0.08 (300 K) to 0.16 (850 K).[25] Figure 2 shows that L is at most ~26% lower than that of the SPB-APS and Eq. (1) results over the entire range of temperatures. In other words, κ_L estimates will maintain the order: $\kappa_{L,deg} < \kappa_{L,SPB-APS} < \kappa_{L,SKB-APS}$ with the largest errors being for the degenerate limit when applied in the non-degenerate case.[22]

Alternative scattering mechanisms can also yield deviations from the SPB-APS. For example, when ionized impurity scattering dominates ($\lambda = 2$), the L actually increases with increasing S; however, this example is not particularly prevalent in materials which have high dielectric constants (including the lead chalcogenides)[26] or at high temperatures. However, when the ionized impurity scattering and acoustic phonon scattering are both considered, the deviation from the SPB-APS is not significant ($Si_{0.8}Ge_{0.2}$ in Table I)–although limited data is available. For $ZrNiSn_{0.99}Sb_{0.01}$ (Table I), acoustic phonon scattering and two other scattering mechanisms (polar and alloy scatterings) are taken into account; these result in a larger deviation as the Seebeck becomes larger. At low temperatures (<100 K), as S approaches zero, it is expected that L converges to the degenerate limit regardless of carrier scattering mechanism[7] and parabolicity of bands involved in transport.[22] However, a pronounced inelastic electron-electron scattering due to high mobility of carriers decreases L from the degenerate limit, even for strongly degenerate materials. In case of n-type PbTe, L at 100 K is approximately 40% lower than its value at 300 K.[24]

Multiple band behavior (present in p-type $PbTe_{0.85}Se_{0.15}$ and n-type $Si_{0.8}Ge_{0.2}$, Fig. 2) can also lead to deviations in the thermopower-dependence of the Lorenz number. In the case of PbTe, hole population of both the light and heavy bands yields a more complicated relationship between L and S; it is not simply a parametric function of η and depends on the specific effective mass and mobility contributions from each band.

One last, prevalent source of error occurs because the Wiedemann-Franz law does not take the bipolar thermal conductivity into consideration. κ_L calculated from the difference between κ_{Total} and κ_E does include varying portion of bipolar conduction with respect to temperature and band structure of materials (which can become important for lightly doped materials with narrow gaps at high temperatures[27]).

An equation for L entirely in terms of the experimentally determined S is proposed and found to be accurate (within 20%) for most common band structures/scattering mechanisms found for thermoelectric materials. Use of this equation would make estimates of lattice thermal conductivity much more accurate without requiring additional measurement. Therefore, zT improvement due to lattice thermal conductivity reduction can be calculated with much improved accuracy and access.

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